2 Hypotheses of Causes of the Ozone Weekend Effect

This chapter presents various “hypothetical” explanations of the ozone weekend effect. Much of the available data have been reviewed by ARB staff and tested against the hypotheses to assess which ones are consistent with the data and, therefore, plausible. Conclusions in this regard are given in Chapter 5 of this report.

Explaining the ozone weekend effect, whether qualitatively or quantitatively, is a difficult task. It is difficult because ozone formation in the lower atmosphere is a highly complex process. Therefore, it is not surprising that multiple rational explanations might cause or contribute to the ozone weekend effect and be proposed.

Multiple rational explanations compound the decision-making difficulty, because data required to discern which explanation(s) are correct are sometimes not available. Although California’s databases for emissions and air quality are among the most extensive in the world, they were designed to address conditions on “typical” days or “episode” days, rather than differences between days of the week. Work is underway to extend these databases to include the needed information.

Six possible causes (hypotheses) of the ozone weekend effect are discussed. The hypotheses consider temporal, spatial, and compositional changes in emissions from weekdays to weekends and how they might interact with meteorological and photochemical processes to create the observed weekday to weekend variation in ozone concentrations. The six hypotheses presented are: 1) NO_X-reduction (a change in the photochemical regime), 2) NO_X-timing (a change in the timing of emissions into the photochemical cycle), 3) carryover near the ground (an increase in the amount of ozone precursors available at sunrise), 4) carryover aloft (an increase in the impact of aged photochemical products mixed down to ground level), 5) increased weekend emissions (an increase in the amount or reactivity of emissions), and 6) soot and sunlight (a decrease in soot emissions which, because they absorb ultraviolet light, allows more ultraviolet light to drive various photochemical reactions). No hypothesis necessarily precludes any other; each could contribute to the ozone weekend effect to a greater or lesser degree. Each hypothesis is considered separately rather than jointly because each has a distinct mechanism and may have different implications with respect to strategic, regulatory NO_X reductions.

Details and expected, “hypothetical” observations

In this section, we address the six hypotheses in detail. First, we present underlying theory that supports each hypothesis. Second, we consider what might be found in real-world data if the hypothesis is correct.

Hypothesis #1: NO_X-reduction

- **Synopsis**

The NO_X-reduction hypothesis presumes that NO_X reductions lead to an ozone "disbenefit" in areas that are "VOC-limited." When ozone formation is VOC-limited, laboratory experiments and air quality models indicate that <u>reducing</u> NO_x emissions may lead to <u>higher</u> ozone concentrations (see Figure 2-1). This counter intuitive effect occurs because the hydroxyl radicals that are an essential part of ozone-forming reactions are "scavenged" by NO_2 to form nitric acid, which traditionally has been thought to irreversibly remove NO_X from the ozone formation process.

The NO_X-reduction hypothesis further presumes that most areas of the South Coast Air Basin are VOC-limited and that NO_X emissions decrease on weekends relatively more than VOC emissions decrease. Therefore, the ratio of VOC to NO_x in the ambient air must be greater on weekends compared to weekdays, and ozone formation might no longer be VOC-limited. If no longer precursor-limited, ozone concentrations on weekends would be higher than ozone on weekdays in the SoCAB.

- **Theory**

Influence of the VOC/NO_x ratio on ozone

Oxides of nitrogen ($NO_X = NO + NO_2$) and volatile organic compounds (VOCs) are both needed to form significant amounts of ozone in the troposphere. They are the key primary pollutants that participate in the photochemical reactions that produce ozone.

The photochemical production of ozone from VOCs and NO_X has been studied extensively. More than 20 years ago, laboratory experiments demonstrated that the ratio of VOC to NO_X is an important factor in determining the maximum ozone generated from initial concentrations of these precursors. The VOC to NO_X ratio that produces the maximum ozone concentration is typically 8 to 10 (Figure 2-1).

When the ratio of VOC to NO_X is greater than 8 to 10, the amount of NO_X tends to limit the amount of ozone formed. In such situations, the ozone producing system is called NO_X-limited or NO_X-sensitive. Under NO_X-sensitive conditions, we expect NO_X reductions to reduce ozone and we expect VOC reductions to have a slight beneficial effect on peak ozone concentrations.

When the VOC to NO_X ratio is less than 8 to 10, the amount of VOCs limits the amount of ozone formed. In such situations, the ozone producing system is called VOC-limited or VOC-sensitive. Under VOC-sensitive conditions, we expect VOC reductions to reduce maximum ozone but we expect NO_X reductions to have a slight to significant negative effect on ozone concentrations depending on the amount of ozone precursors present (i.e., may cause the maximum ozone produced to increase).

The simple “EKMA” diagram shown in Figure 2-1 illustrates these two general conditions (adapted from Finlayson-Pitts and Pitts, 2000, pg. 898).

The shape of the ozone isopleths in an EKMA diagram occurs because NO_X participates in reactions that compete with one another. While NO_X ($NO + NO_2$) participates in atom-producing and radical-producing reactions that enhance ozone formation, it also participates in radical terminating or “quenching” reactions that retard ozone formation.

Thus, for example, NO_2 absorbs solar ultraviolet radiation and dissociates into NO and an oxygen atom. The oxygen atom may then react with an oxygen molecule to form ozone. Conversely, NO_2 molecules react rapidly with hydroxyl radicals to for relatively “stable” nitric acid (HNO_3), thus reducing the number of NO_2 molecules available for further ozone-producing reactions.

Radical-producing reactions include photolysis of nitrogen dioxide:

$$\mathbf{NO_2 + (ultraviolet)h\nu \rightarrow NO + O(radical)}$$

The following reaction creates ozone:

$$\mathbf{O + O_2 \xrightarrow{M} O_3}$$

The following is a radical-terminating reaction:

$$\mathbf{NO_2 + OH(radical) \rightarrow HNO_3(g)}$$

Fresh NO_X emissions (primarily as NO) scavenge or destroy O_3 by the following rapid reaction:

$$NO + O_3 \rightarrow NO_2 + O_2$$

The presence of organic radicals are necessary to increase O_3 concentrations to unhealthful levels. They do so because O_3 is not destroyed in the process of creating an NO_2 molecule (as in the previous equation):

$$NO + RO_2\bullet \rightarrow NO_2 + RO\bullet$$

Thus, in a given air parcel, the relative balance of organic compounds and (NO_X (e.g., VOC/NO_X ratio) helps determine whether the available NO_X behaves as a net ozone generator or a net ozone inhibitor.

In recent years in the South Coast Air Basin, most measured VOC/NO_X ratios are less than eight. Average VOC/NO_X ratios on weekends are approximately 10-20 percent higher on Saturday and 20-30 percent higher on Sunday compared to weekdays, though measured VOC/NO_X ratios on weekdays and weekends vary greatly and their ranges overlap substantially.

Emissions in the SoCAB on weekends and weekdays

The NO_X-reduction hypothesis asserts that present-day emissions patterns in the South Coast Air Basin cause conditions in most locations to be VOC-limited on both weekdays and weekends; that is, the VOC/NO_X ratios are generally less than 8. Furthermore, the hypothesis assumes that NO_X is reduced on weekends substantially more than VOCs are reduced. Consequently, the weekend VOC/NO_X ratio is higher than the VOC/NO_X ratio on weekdays and this causes the higher ozone concentrations on weekends as implied by the EKMA diagram in Figure 2-1.

Measured concentrations of VOCs and NO_X in the South Coast indicate that weekend NO_X reductions are proportionally greater than VOC reductions.

Motor vehicles are a major source of NO_X emissions, with heavy-duty diesel trucks producing a disproportionate share of the total NO_X emissions (~30% of total). Traffic activity data in the South Coast Air Basin indicate that heavy-duty trucks are much less active on weekends compared to weekdays (see Chapter 5 in the Technical Support Document). With respect to the daily total volume of heavy-duty trucks, Sunday activity levels are approximately 60 to 80 percent less than weekday levels.

- **Hypothetical expectations**

If the NO_X-reduction hypothesis contributes substantially to the weekend effect, we might (hypothetically) expect to observe the following:

- Typical VOC/NO_X ratios on weekdays and on weekends should (hypothetically) be less than eight, which would indicate VOC-limited conditions.

- Because NO_X is (hypothetically) reduced on weekends more than VOCs, the VOC/NO_X ratio on weekends should be higher than on weekdays for the same period of the day.

- Ozone concentrations should (hypothetically) increase earlier on weekends than weekdays because radicals are more likely to participate in ozone-forming reactions and less likely to react with NO_2.

- The NO_2 to NO ratio should (hypothetically) be higher on weekends than weekdays because the photochemical system is more active and produces more radicals that convert NO to NO_2 more rapidly.

Hypothesis #2: NO_X-timing

- **Synopsis**

The NO_X-timing hypothesis presumes that the timing of emissions on weekends plays a major role in determining the weekend effect. In particular, the NO_X-timing hypothesis asserts that the timing of NO_X emitted on weekends into a mature photochemical system causes these emissions to produce ozone more efficiently compared to the NO_X emitted on weekdays.

The NO_X-timing hypothesis further assumes that NO_X emissions for several hours following sunrise are much lower on weekends (less commute traffic, etc.) compared to weekdays but increase substantially around mid-day. Because less NO_X is present to depress the concentration of radicals, the photochemical system becomes more active earlier in the day. As activities and emissions increase toward mid-day, the fresh NO_X enters this more active system, participates in ozone-generating reactions more efficiently, and leads to higher weekend ozone compared to weekdays.

- **Theory**

Influence of NO_X timing on ozone

The NO_X-timing hypothesis differs from the NO_X-reductions hypothesis in the pattern of "relative reductions." The NO_X-timing hypothesis says that large reductions in NO_X emissions from 6 a.m. to 10 a.m. followed by small reductions from 11 p.m. to 3 p.m. produces more ozone compared to reductions in NO_X emissions by a uniform proportion for all hours of the day. [Note: Most NO_X control measures would result in uniform proportional reductions for all hours.]

The distinction between the NO_X-reduction hypothesis and the NO_X-timing hypothesis concerns the dashed (future weekdays) and dotted (current Sundays) lines in Figure 2-4. The NO_X-reduction hypothesis asserts that the hourly emissions profile represented by the dashed line produces the same ozone maximum as the hourly emissions profile represented by the dotted line. The NO_X-timing hypothesis, on the other hand, asserts that the dotted-line profile produces a higher ozone maximum compared to the dashed-line profile. This difference is important because the two hypotheses have substantially different policy implications with respect to NO_X controls as an ozone control measure.

Laboratory experiments show that the timing of NO_X emissions can strongly affect the amount of ozone produced. When NO_X emissions enter an active photochemical system, they appear to be more efficient at producing ozone compared to NO_X emissions that enter a less active (mature) system. Figure 2-2 (adapted from Figure 4 in Hess, *et al*., 1992) illustrates the effect of the timing of NO_X emissions for ozone formation efficiency.

According to Figure 2-2, NO_X and VOCs are present as the sun begins to rise. As sunlight increases, photochemical reactions increase and the system moves through a "light-limited" phase toward a "NO_X-limited" phase. When a fresh dose of

NO_X is injected into this system, ozone production does not decrease but increases to a higher NO_X-limited plateau.

The VOC to NO_X ratio typically increases from morning through the late afternoon. This happens because VOCs persist in the atmosphere longer than NO_X. The NO_X is transformed relatively quickly into other compounds; some of these reaction products, such as nitric acid, have traditionally been assumed to participate little in ozone forming processes. Therefore, even VOC-limited systems tend to move from their initial VOC-limited conditions toward NO_X-limited conditions as the daylight hours progress (Lu and Chang, 1998).

The NO_X-timing hypothesis assumes that the photochemistry on weekends is more efficient compared to weekdays during mid-day hours when the NO_X and VOC emissions increase sharply compared to the morning hours. Although VOC and NO_X emissions on weekends are smaller, the emissions are comparable to emissions on weekdays during the peak UV radiation period. They produce more ozone because they are emitted into a more "primed" photochemical system (i.e., the VOC/NO_X ratio is no longer VOC-limited and, if NO_X-limited, has plenty of NO_X for ozone formation.

Timing of NO_X emissions in the SoCAB on weekends and weekdays

According to the preceding theory, if weekend activity patterns delay NO_X emissions, the ozone production from mid-day NO_X emissions may be more efficient and generate more ozone on weekends than on weekdays. Furthermore, a delay in the diurnal pattern of NO_X emissions may cause ozone to increase even when the total NO_X emissions are lower because the advance photochemistry has driven the system toward the NO_X-limited regime.

The NO_X-timing hypothesis proposes that NO_X emissions are much lower on weekends than on weekdays for several hours immediately following sunrise. Afterwards, however, NO_X-producing activities increase substantially and put fresh NO_X emissions into a photochemical system that is more active (efficient) compared to weekdays. Figures in Section 5.3 of the Technical Support Document indicate that ambient NO_X concentrations in the SoCAB at sunrise on Saturday and Sunday are often much lower compared to weekdays, but are closer to the weekday levels by mid-day.

On-road motor vehicles constitute the largest single source of NO_X emissions in the SoCAB (see Table 1 in Chapter 1). Some emission inventories attribute approximately two thirds of NO_X to on-road cars and trucks. Initial analyses of traffic data on freeways indicate that the timing of weekend activity and, therefore, emissions may be much different from the timing of weekday activity and emissions (see Chapter 5.2 of the Technical Support Document). Figure 2-4 illustrates likely weekday/weekend differences in the timing of total NO_X emissions from all sources.

- **Hypothetical expectations**

If the NO_X-timing hypothesis contributes substantially to the weekend effect, we might (hypothetically) expect to observe the following:

- The total activity of major NO_X sources should (hypothetically) be much lower on weekend mornings than on weekday mornings, but total NO_X emissions near mid-day should be closer to weekday activity though not necessarily equal. This is the basic reason for a difference in the timing of NO_X emissions on weekends compared to weekdays.

- If an effect due to NO_X timing occurs independently of effects due to lower total NO_X emissions, then ozone should (hypothetically) be higher than expected on weekends everywhere, even in NO_X-limited regions. In such regions, ozone is expected to decrease with lower NO_X. However, NO_X-timing effects on weekends, rather than lower total NO_X, could prevent ozone from decreasing as much as expected in NO_X-limited regions.

- VOC/NO_X ratios should (hypothetically) be higher on weekend mornings compared to weekday mornings. This is because NO_X decreases proportionally more (hypothetically) on weekends between 6 a.m. and 10 a.m. compared to decreases in VOCs.

- NO_2 to NO ratios on weekends should be higher than on weekdays. Because fresh NO emissions are (hypothetically) much lower during the typical morning commute hours, a larger fraction of the NO will (hypothetically) be converted to NO_2 by ozone and radicals.

Hypothesis #3: Carryover near ground-level

- **Synopsis**

The hypothesis concerning carryover near ground level does not involve complex theory. It simply asserts that the higher weekend ozone concentrations occur because extra emissions from traffic on Friday and Saturday nights participate in ozone formation during the daylight hours that follow. How would such a situation occur?

This hypothesis asserts the nocturnal boundary layer plays an important role in determining the weekend effect. The nocturnal boundary layer is a layer of cool air that forms at ground level and remains there as radiant cooling takes place overnight (see

Figure 2-3).

This hypothesis further presumes that traffic is higher on Friday night and Saturday nights compared to other nights. The increased traffic causes additional emissions of VOCs and NO_X to be injected into the nocturnal boundary layer. These extra emissions of ozone precursors then carry over and lead to greater ozone formation after sunrise on the following day.

- **Theory**

Influence of meteorology on emissions at the surface

Sometime after mid-day and before sunset, the radiant energy going out from the Earth's surface exceeds the incoming radiant energy. At that point, the surface and the air near the surface begin to cool. Vertical mixing of the air due to convection ceases when the potential temperature (as if the air was at sea-level pressure) of the air near the ground is lower than the potential temperature of the air above it.

The cooling process continues overnight as infrared radiation dissipates heat from the surface. As shown in

Figure 2-3, a nocturnal boundary layer (NBL) is the result. This layer of air is stable and remains near the surface. Although some turbulent mixing may continue to take place at night, such mixing is commonly limited to a relatively shallow layer.

Emissions and traffic in the SoCAB

The hypothesis concerning carryover near the ground states that traffic increases in the SoCAB on Friday and Saturday nights relative to other nights of the week. Although traffic data for surface streets are scarce, data for freeways indicate that traffic does indeed increase on Friday and Saturday nights.

Depending on the mix of vehicles, the composition of the emissions injected into the NBL on Friday and Saturday nights may be different from the usual composition. If light duty vehicles increase relative to heavy-duty diesel vehicles, the emissions that carryover to the following day may be especially rich in VOCs and less rich in NO_X. The currently available data are not sufficient to resolve such considerations at this time.

- **Hypothetical expectations**

If this hypothesis contributes substantially to the weekend effect, we might (hypothetically) expect to observe the following:

- Total traffic on Friday and Saturday nights should (hypothetically) be greater than the total traffic on other nights.

- At sunrise, ambient concentrations of VOCs and NO_X should generally be greater on Saturday and Sunday compared to other days (hypothetically).

Hypothesis #4: Carryover Aloft

- **Synopsis**

According to the carryover aloft hypothesis, a reservoir of pollutants usually carries over from one day to the next above the nocturnal boundary layer (see). This reservoir can be large and rich in ozone, VOCs and possibly radicals in stable forms during the night (e.g., HONO). These pollutants represent a legacy from the emissions and other conditions that prevailed "yesterday." Nevertheless, these pollutants carry over (overnight), mix down to the surface the next day, and affect ground-level ozone measurements "today."

The carryover aloft hypothesis presumes that significant carryover aloft occurs on all days of the week, but pollutants that carry over aloft exert a greater influence on surface ozone concentrations on weekends than they do on weekdays. On weekdays, large amounts of fresh NO_X emissions titrate or "quench" the ozone and radicals that carry over so they have little effect on surface concentrations. On Saturday and Saturday however, NO_X emissions are reduced substantially and ozone and radicals that carry over aloft are not fully quenched by the fresh emissions on weekends and thus cause ozone concentrations at the surface to be higher on weekends compared to weekdays.

- **Theory**

Meteorology and carryover of pollutants aloft

When the nocturnal boundary layer (NBL) develops at the surface overnight (see the previous hypothesis concerning carryover near the ground), a large reservoir of pollutants may be sequestered above it (Zhao and Hardesty, 1999). This reservoir may begin less than one hundred meters above the ground and end 1500 meters of more above the ground. In this discussion, the layer of air above the NBL is referred to as "aloft." Pollutants that carry over aloft may have a strong effect on surface ozone measurements the following day (Zhang and Rao, 1999).

At sunrise, the air aloft is usually isolated from the NBL due to a surface-based temperature inversion. As the sun rises, the Earth's surface warms and in turn warms the air near it. The warm air rises and exchanges places with air from aloft. This convective mixing erodes the temperature inversion, and pollutants aloft mix down to the surface, a process called fumigation. In this way, ozone and other pollutants that carry over aloft can interact with fresh emissions and may strongly affect today's ground-level ozone concentrations.

Nature and chemistry of pollutants aloft

Measurements taken during special studies in the SoCAB show that high concentrations of ozone (60 to 120 ppb or even more) can persist aloft throughout the night. Measurements using LIDAR (Zhao and Hardesty, 1999), airplanes (Anderson and Blumenthal, 1999), and balloons (Fitz, 1998) indicate that a large reservoir of pollutants aloft may be routine rather than unusual in the SoCAB.

Additional measurements aloft, such as VOCs and NO_Y (total reactive nitrogen), indicate that conditions for ozone formation aloft may be strongly NO_X-limited (Anderson and Blumenthal, 1999). As discussed under the NO_X-timing hypothesis, conditions tend to shift from VOC-limited to NO_X-limited over time; surface measurements demonstrate that this transition occurs as air parcels travel downwind horizontally, away from NO_X sources. In essence, the air aloft has traveled "downwind" vertically rather than horizontally and has become NO_X-limited (Sillman, 1999).

Only trace amounts of NO occur aloft so almost all NO_X aloft is in the form of NO_2. Measured amounts of "NO_x", however, often include other compounds, such as PAN, that readily contribute to ozone-forming reactions. As the day unfolds, the mixing layer deepens, and fresh NO_X emissions from the surface interact with pollutants from aloft. The mixing of aged pollutants aloft, especially ozone, with fresh NO emissions will destroy ozone and convert the NO to NO_2.

Emissions in the SoCAB on weekdays and weekends

With respect to emissions, the carryover aloft hypothesis asserts that weekend emissions during the initial hours of photochemical activity are substantially lower than weekday emissions. Therefore, the NO_X-limited carryover from aloft can exert a proportionally greater influence on weekend ozone levels than it does on weekday ozone levels.

On weekends, the mixing of aged pollutants with a smaller body of fresh emissions causes the fresh NO_X emissions to be more efficient at producing ozone. This phenomenon is similar to that described under the NO_X-timing hypothesis.

In addition, the carryover aloft hypothesis states that more of the ozone carried over aloft is measured at the surface on weekends compared to weekdays. On weekdays, large amounts of fresh NO_X emissions destroy or "quench" the ozone and radicals that carry over and limit their contribution to surface ozone measurements. On weekends, however, fresh NO_X emissions are greatly reduced, less of the ozone from aloft is destroyed, and more of the ozone that carried over is measured at the surface. The situation is further enhanced on Sunday when presumably more ozone aloft is carried over from Saturday and fresh NO_X emissions on Sunday are even lower during mid-morning (weekday commute period) than on Saturday.

- **Hypothetical expectations**

If this hypothesis contributes substantially to the weekend effect, we might (hypothetically) expect to observe the following:

- The photochemical system aloft should (hypothetically) be NO_X-limited.

- The mix of VOCs during the hours leading up to the ozone maximum should (hypothetically) be "older" on weekends compared to weekdays. To see this, however, the whole spectrum of VOC species including the products of reactions in the atmosphere must be measured, not just species characteristic of fresh emissions.

- Large reservoirs of ozone and ozone precursors aloft should (hypothetically) be the norm rather than the exception.

- Pollutants aloft should (hypothetically) begin to mix with the NBL some hours before the ozone maximum.

- Measured NO_X concentrations should (hypothetically) be relatively large on weekdays and relatively small on weekends during the hours when convective mixing begins.

- Hypothetically, carryover contributes similar amounts of ozone and peroxy-radicals on weekdays and weekends, but substantially less NO is emitted on weekends. Consequently, a larger fraction of the weekend NO emissions would be converted to NO_2 by the relatively larger amount of ozone and peroxy radicals available via carryover aloft. Therefore, the NO_2 to NO ratio would (hypothetically) be higher on weekends than on weekdays, at least until the carryover effects reaches a maximum for the day.

Hypothesis #5: Increased weekend emissions

- **Synopsis**

According to the increased weekend emissions hypothesis, higher weekend ozone levels in at least some locations are caused by increased emissions and/or increased reactivity of VOC emissions from activities that occur more often on weekends than on weekdays.

The increased weekend emissions hypothesis further proposes that the total emissions of VOCs and/or NO_X in some areas of the SoCAB increase on weekends rather than decrease; increased emissions then lead to local increases in ozone on weekends. Suburban residential regions and areas with high levels of recreational activity are prime candidates for these phenomena.

- **Theory**

According to the increased weekend emissions hypothesis, higher weekend ozone levels are caused by increased emissions or more reactive emissions on weekends. That is, some activities take place predominantly on weekends and emissions from these activities <u>more than offset</u> any reductions in activities that decrease on weekends.

If this hypothesis is relevant to more than a few locations, then some significant and ubiquitous sources of ozone precursors must increase their activities substantially on weekends. At least two emission categories – diurnal evaporative emissions from motor vehicles and emissions from home maintenance activities, such as painting and lawn and garden activity – may increase on weekends and qualify as significant and ubiquitous.

Weekend increases in emissions are likely to emphasize VOCs rather than NO_X. Activities such as lawn and garden care and recreational boating, for example, are relatively rich in VOC emissions and can produce large amounts of emissions for several reasons (relatively loose standards, poor maintenance, age, etc.).

Although this hypothesis may not apply generally, ozone at selected sites might reflect local increases in precursors due to weekend increases in some activities.

- **Hypothetical expectations**

If this hypothesis contributes substantially to the weekend effect, we might (hypothetically) expect to observe the following:

- Comparisons of weekday-specific and weekend-specific emission inventories should (hypothetically) identify increased emissions or increased reactivity of emissions on weekends.

- Ambient concentrations of VOCs and/or NO_X should be greater on weekends compared to weekdays at more than a few sites.

- The Weekend Effect should exhibit regional/local patterns in areas with high recreational activities.

Hypothesis #6: Soot and sunlight

- **Synopsis**

This hypothesis presumes that the amount of soot or elemental carbon particles in the atmosphere is greater on weekdays than on weekends. Furthermore, this difference strongly affects ozone formation because soot absorbs ultraviolet sunlight that would otherwise participate in ozone-forming processes.

Hypothetically, large numbers of vehicles, including heavy-duty diesel trucks, emit soot on weekdays. On weekends, however, traffic is greatly reduced and less soot is emitted. The lower soot concentrations on weekends absorb less ultraviolet sunlight, which in turn increases ozone formation on weekends. Thus, reduced soot contributes to higher ozone concentrations on weekends compared to weekdays.

- **Theory**

Actinic flux

Ultraviolet light of specific wavelengths is needed to initiate the processes that form ozone in the troposphere. The total amount of photochemically active light that passes through a part of the atmosphere is called the “actinic flux.” The actinic flux arrives from all directions.

Particles and actinic flux

Sometimes, the presence of particles in the air can increase actinic flux by scattering ultraviolet light. When light scatters, it usually travels a longer path in the atmosphere before being absorbed, passing through the atmosphere, or being reflected back out to space. Therefore, the total number of ultraviolet photons in a particular volume of air may increase.

Soot particles, on the other hand, decrease actinic flux by absorbing ultraviolet light. When soot absorbs ultraviolet light, the energy is typically re-radiated as infrared photons, which do not initiate ozone-forming chemical reactions.

Emissions and particles

According to the soot and sunlight hypothesis, soot-producing activities are greatly reduced on weekends. On-road motor vehicles are a major source of soot, and vehicle traffic on weekends is (hypothetically) reduced substantially on weekends, at least during the morning hours. Therefore, emissions of soot are much lower (hypothetically) on weekends compared to weekdays.

Because more ultraviolet light is (hypothetically) available on weekends, smog-forming photochemistry is more active and ozone is higher on weekends compared to weekdays.

- **Hypothetical expectations**

If this hypothesis contributes substantially to the weekend effect, we might (hypothetically) expect to observe the following:

- Comparisons of vehicle activity on weekdays and weekends should (hypothetically) show large decreases on weekends.

- Ambient levels of soot should (hypothetically) be significantly smaller on weekends compared to weekdays.

- Measurements of actinic flux at the surface or within the mixing layer should (hypothetically) be greater on weekends compared to weekdays.

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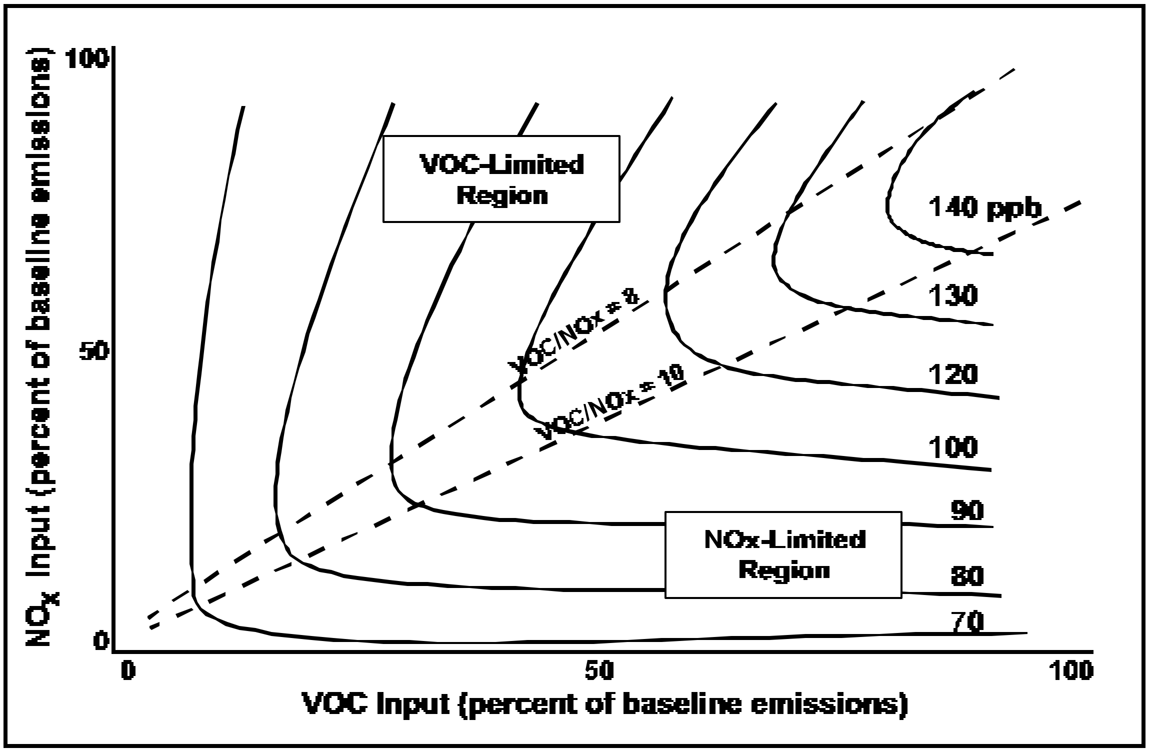
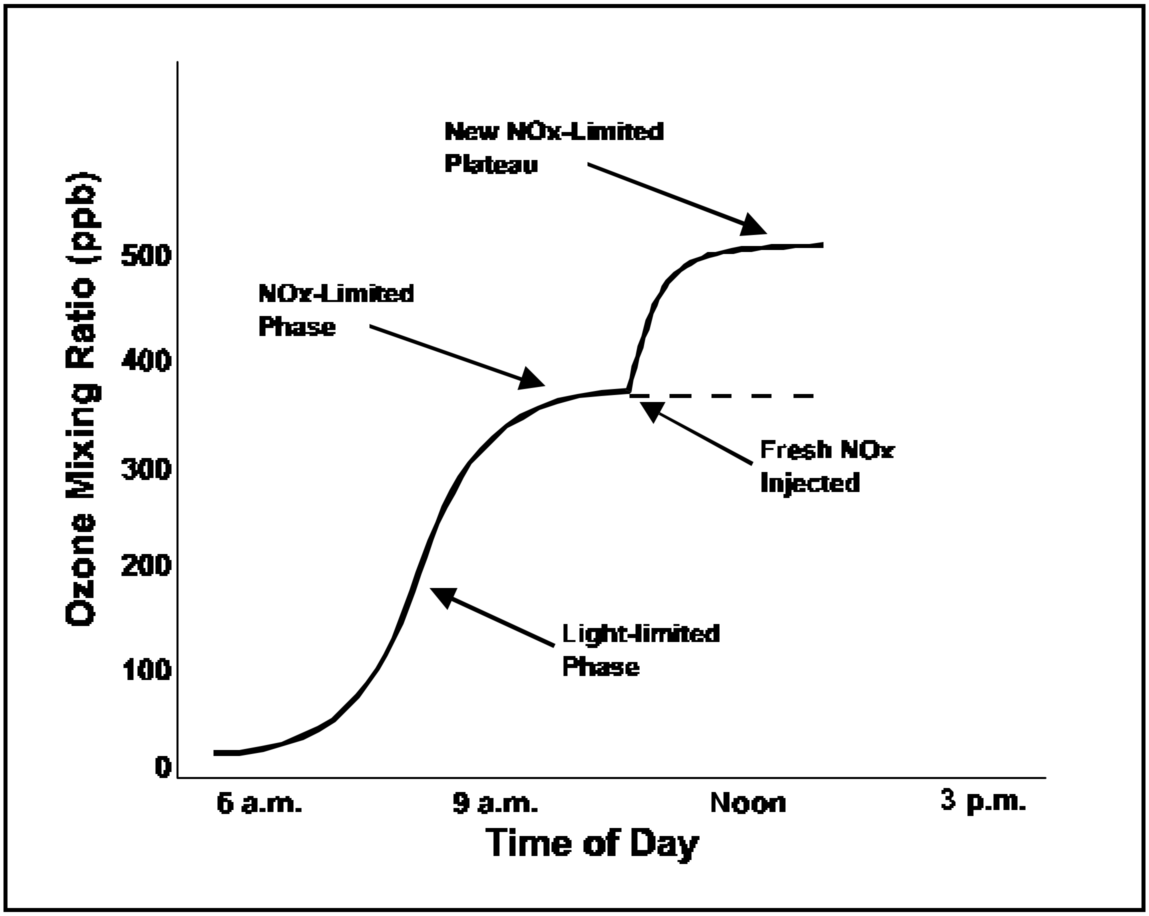
Figure 2-1. Schematic EKMA diagram illustrating the relationship between the initial concentrations of VOC and NO_X and the resulting maximum ozone concentration (part per billion).



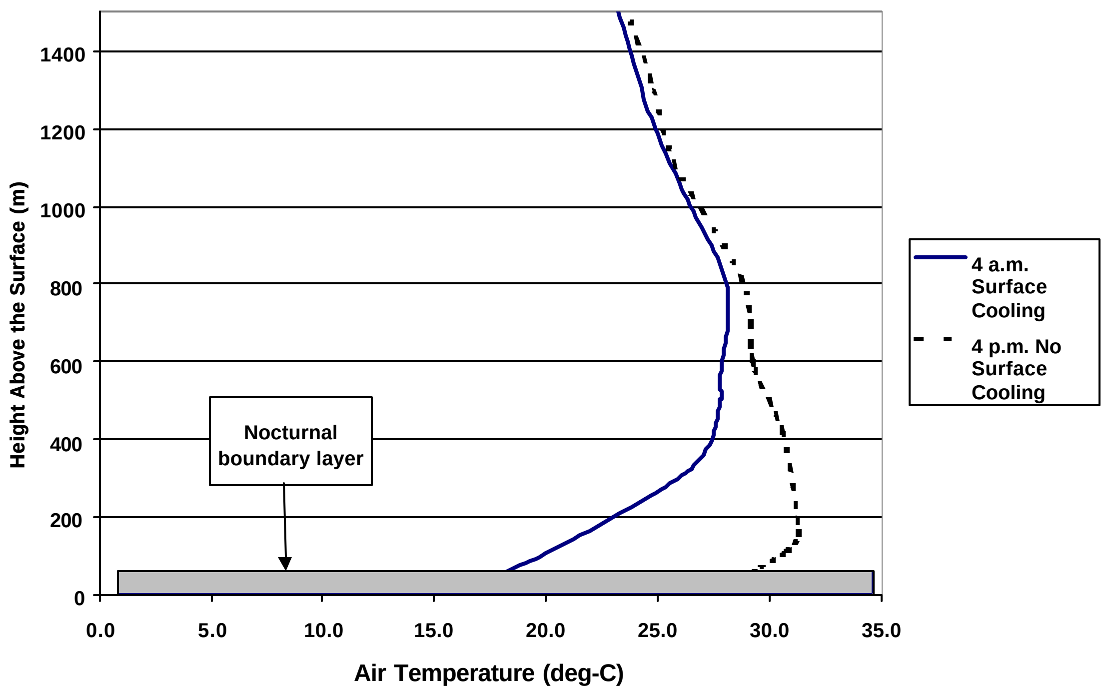
Source: Adapted from Winner, Cass, and Harley (1995)
as presented in Finlayson-Pitts and Pitts (2000), page 898.

Figure 2-2. Illustration of NO_X timing effect in the laboratory.



Source: Adapted from Figure 4 in Hess, et al., 1992
Mixing ratios are large because this was a smog chamber experiment.

Figure 2-3. Examples of soundings at 4 a.m. and 4 p.m. at Oakland, California, illustrating surface cooling after sunset and before sunrise. Cooling results in a surface-based inversion. In this case, overnight carryover of pollutants may include nighttime emissions trapped below 200 m and a large reservoir of yesterday's daytime primary and secondary pollutants sequestered above 200 m.



Note: Figure created using data from soundings taken at Oakland International Airport.

Figure 2-4 Comparison of hypothetical hourly emission profiles before and after NO_X control; profiles for current weekday and Sunday reflect traffic data.